PATENT

APPLICATION{PRIVATE }

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF

HERBERT EICHENAUER

SERIAL NUMBER: 09/997,952

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TITLE: THERMOPLASTIC MOLDING COMPOSITIONS

DECLARATION

I, Herbert Eichenauer, a Citizen of Germany, hereby declares as follows:

That I am the inventor named in U.S. Patent Application Serial Number 09/997,952, that was filed November 30, 2001; and

That I have studied Chemistry and hold a doctorate degree conferred upon me by the University of Giessen, Germany; and

That I have been in the employ of Bayer AG, the assignee of the captioned patent application since 1980, holding responsible positions in research and developments of polymeric compositions; and

That I have authored three technical publications and been awarded more than 100 patents relating to my field of expertise; and

That I have read and understood the Office Action dated June 18, 2003 that issued in the prosecution of the captioned Patent Application and the cited U.S. Patent 5,236,911 to Koyama (herein the Koyama document); and

That I have calculated the glass transition temperature of the copolymer described in column 6, lines 25-33, of the Koyama document (herein "the Relevant Copolymer"); and

That my calculation of the Glass transition temperature was based on Fox's equation

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

where T_g is the glass transition temperature of the resulting copolymer, W_1 and W_2 are respectively the weight fractions of the individual monomers and T_{g1} and T_{g2} are glass transition temperatures of the respective individual homopolymers, the equation being a relationship known in the art, having been published in Bull. Am.Phys. Soc. 1956, 1, 123 (copy enclosed); and

That, in my calculation, I have relied for the glass transition temperatures of MMA and EA on (POLYMER HANDBOOK, Third Edition (J. Brandrup, E.H. Immergut), Wiley Interscience, New York, 1989) (copy of the relevant pages are enclosed) and that I approximated the glass transition of poly-AMA to be about 293°K.

That my calculation leads me to conclude that the glass transition temperature of the Relevant Copolymer is about 368°K = 95°C, that is in any event significantly higher than 0°C.

The undersigned Declarant declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States code and that such willful false statements may jeopardize the validity of pending Application Serial Number .09/997,952 or any patent issuing thereon.

Signed at Dormagen this 5th day of November, 2003.

Herbert Eichenauer

s:\ksl\6482declaration

J4. Effect of Light Scattering upon the Apparent Refractive Ind x of Dispersed P lymers.* M. NAKAGAKI AND W. HELLER, *Wayne University*.—Precise determinations of particle size and molecular weight of polymer spheres by means of the Mie theory requires that the refractive index of the light scattering material is accurately known. An experimental determination of the refractive index, using any of the existing mixture rules proved inadequate unless the results obtained are extrapolated to zero-particle size.[1] At all finite particle sizes, the refractive index obtained is only an apparent quantity due to complications arising from both forward and backward scattering. Following recent work by Zimm and Dandliker,[2] concerned with the effect of forward scattering upon the Rayleigh ratio, the theoretical variation of the apparent refractive index was established as a function of the theoretical forward scattering as derived from the Mie theory. The computations were carried out for a series of relative refractive indices up to 1.30 and for α values up to 8.0, covering herewith the entire submicroscopic range. The theoretical data obtained fit very satisfactorily the experimental data referred to above.

* This work was supported by the Office of Naval Research.
[1] W. Heller and T. L. Pugh, paper presented before the Division of Polymer Chemistry at the 128th meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955.
[2] B. H. Zimm and W. B. Dandliker, J. Phys. Chem. 58, 644 (1954).

J5. Influence of Diluent and of Copolymer Composition on the Glass Temperature of a Polymer System. T. G. FOX, *Rohm & Haas Company*.—A relationship for the dependence of the glass temperature on composition for a copolymer or a plasticized polymer may be derived from simple assumptions. In the limiting form it becomes

$$\frac{1}{T_g}=\frac{w_1}{T_g(1)}+\frac{w_2}{T_g(2)}.$$

For a plasticized polymer $T_g(1)$ and $T_g(2)$ represent the glass temperatures of the pure polymer and pure diluent, and w_1 and w_2 are their respective weight fractions in the mixture. For a copolymer, w_1 and w_2 refer to the weight fraction of the two comonomers, whereas $T_g(1)$ and $T_g(2)$ refer to the glass temperatures of the two corresponding homopolymers. This equation may be expected to apply to systems which are compatible and not too strongly polar. Data on copolymers and on polymer-diluent systems illustrate that this is substantially true.

J6. Glass Temperatures of Poly-(Chlorotrifluoroethylene), Poly-(Vinylidene Fluoride), and their Copolymers.* L. MANDELKERN, G. M. MARTIN, AND F. A. QUINN, JR., *National Bureau of Standards*.—The glass temperatures of poly-(chlorotrifluoroethylene), poly-(vinylidene fluoride), and five of their copolymers of varying composition were determined using volume dilatometers and an automatic recording interferometer. The glass temperatures for the two homopolymers were found to be in the range +30° to 35°C for poly-(chlorotrifluoroethylene) and −25° to −30°C for poly-(vinylidene fluoride). A quenched sheet of poly-(chlorotrifluoroethylene) originally formed by compression molding displayed a 1% increase in thickness on initial heating above 30°C but this phenomenon did not manifest itself on subsequent cooling and heating cycles. The glass temperatures Tg, of the copolymers ranged between the values of the two homopolymers. However, in order for the simple linear relation $1/Tg = w_1/T_{g_1} + w_2/T_{g_2}$ to be obeyed, where w_1 and w_2 are the weight fractions of the two components, and Tg_1 and Tg_2 the glass temperatures of the respective homopolymers, the required glass temperature for poly-(vinylidene fluoride) would be about 15° lower than observed. The effect of crystallization on the glass temperature of a copolymer will also be discussed.

* Supported in part by the Quartermaster Research and Development Command, Rubber Branch.

J7. Dilatometric Measurements on Gels of Cellul se Tributyrate and Cellulose Nitrate. M. N. VRANCKEN AND JOHN D. FERRY, *University of Wisconsin*.—The thermal expansion of gels of cellulose tributyrate in dimethyl phthalate and cellulose nitrate in diethyl phthalate has been studied over a temperature range from 155°K to room temperature, using Pyrex dilatometers with long capillary tubes and 2,3-dimethyl pentane as a confining liquid. Values of the glass transition temperatures (T_g) and of the thermal expansion coefficients above and below T_g have been determined. For cellulose tributyrate gels, T_g decreases with decreasing polymer concentration. Below 20% polymer, measurements became impossible, because of partial freezing out of solvent. For cellulose nitrate, over a concentration range from 37% to 12%, T_g goes through a minimum with decreasing polymer concentration.

J8. Hydrodynamic and Thermal Behavior of a Plastic Column. S. BROERSMA, *Northwestern University*.—The low value of Reynold's number and the low heat conductivity make it necessary to analyze the flow of hot plastic on the basis of a layer system. Thus a roll resting on two calenders, one of which is at rest, can be divided into a center core, an outside layer penetrating the nip and a thin coating sheared off by the web. The observed flow pattern of the longlived core can be understood on the basis of Newtonian hydrodynamics. Taking into account an exponential temperature dependence of the viscosity, instabilities in the temperature are theoretically predicted. The time constant is of the order of an hour. Most of the heat development and force action takes place in the outside layer reaching deep into the nip. The fact that the bare rolls do not allow plastic to pass indicates that the increase in shear stress with depth cannot be matched by outside forces so that sliding does occur. The relationship observed between the force keeping the rolls together and the thickness of the film passing with the web can be explained with a viscosity varying as $(\tau_0/\tau)^n \exp -p/p_0$. In the case of polyethylene, $\tau_0=0.5$ atmos, $n=1$, $p_0=50$ atmos apply. Irregularities in the plastic coating affecting a technical process, can be related to the existence of layers of different temperature.

J9. Kinematographic Study of Tensile Fracture in Polymers. A. M. BUECHE AND A. V. WHITE, *General Electric Research Laboratory*.—High-speed motion pictures were taken of silicone rubber, irradiated polyethylene, Plexiglas II, and aluminum foil while they were being broken. Fractures started internally in some of the silicone samples but at the edges of all of the others. The rates of crack growth and the rates of retraction of the ends of the rubber samples were measured. The velocities with which the cracks grew were compared with the results of the theories of Poncelet and Yoffe. Their prediction, that the velocities should be about one-half those of transverse waves in the media, was found to represent the data for materials with moduli differing by five decades. After fracture, the ends of the rubber samples contracted with velocities approximately equal to the velocities of longitudinal waves in these samples.

POLYMER HANDBOOK

THIRD EDITION

Edited by

J. BRANDRUP and E. H. IMMERGUT

WILEY

A WILEY-INTERSCIENCE PUBLICATION
JOHN WILEY & SONS
New York • Chichester • Brisbane • Toronto • Singapore

Polymer	CAS No.	T_g(K)	Remarks	References
Poly(propylene) *cont'd*		272	DSC, onset, quenched, f (MW)	1081
syndiotactic (c)		~265	most values range 263 to 267 K	
Poly(propylethylene)		~233	Conflicting data	1,272,574,595, 629,630,632,645, 685,727
Poly(propyl-2-propylene)		300	Dynamic method	682
Poly(tetradecylethylene)		246		629,632,641

1.3 Poly(acrylics) and Poly(methacrylics)

1.3.1 Poly(acrylic acid) and Poly(acrylic acid esters)

Polymer	CAS No.	T_g(K)	Remarks	References
Poly(acrylic acid)		379		720,811–818
Poly(benzyl acrylate)		279		746
Poly(4-biphenylyl acrylate)		~383		819
Poly(4-butoxycarbonylphenyl acrylate)		286		746
Poly(butyl acrylate)		219	Mechanical method	1,23,634,775, 820–822
Poly(sec-butyl acrylate) conventional		251		823,824
syndiotactic		253		
isotactic		250		
Poly(tert-butyl acrylate)		380,316,346	Conflicting data	746,824,825
Poly(2-tert-butylphenyl acrylate)		345		826
Poly(4-tert-butylphenyl acrylate)		344		826
Poly(cesium acrylate)		447	Extrapolated from DSC data on water plasticised samples	817
Poly[3-chloro-2,2-bis(chloromethyl)propyl acrylate)		319		746
Poly(2-chlorophenyl acrylate)		326		746
Poly(4-chlorophenyl acrylate)		331		826
Poly(2,4-dichlorophenyl acrylate)		333		746
Poly(pentachlorophenyl acrylate)		420		746
Poly(4-cyanobenzyl acrylate)		317		746
Poly(2-cyanobutyl acrylate)	25154–80–7	384–396	Dilatomer, 10 deg/min HR, DTA, f (polymerization)	1088
Poly(2-cyanoisobutyl acrylate)	26809–38–1	324	Dilatomer, 10 deg/min HR	1089
Poly(4-cyanobutyl acrylate)		233–238	No experimental details	827
Poly(2-cyanoethyl acrylate)		277		746,820
	25067–30–5	388	Dilatomer, 10 deg/min HR	1090
Poly(2-cyanoheptyl acrylate)	26936–29–8	389	DTA	1092
Poly(2-cyanohexyl acrylate)	26877–39–4	358	Dilatomer, 10 deg/min HR	1093
Poly(cyanomethyl acrylate)		433	Dilatomer, 10 deg/min HR, DTA, f (polymerization)	1087
Poly(2-cyanomethyl acrylate)		296	No experimental details	820
Poly(5-cyano-3-oxapentyl acrylate)		250	No measurement details	820
Poly(4-cyanophenyl acrylate)		363		746
Poly(2-cyanoisopropyl acrylate)	25931–02–6	339	Dilatomer, 10 deg/min HR	1091
Poly(4-cyano-3-thiabutyl acrylate)		249		828
Poly(6-cyano-3-thiahexyl acrylate)		215		828
Poly(6-cyano-4-thiahexyl acrylate)		215		828
Poly(8-cyano-7-thiaoctyl acrylate)		214		828
Poly(5-cyano-3-thiapentyl acrylate)		223		828
Poly(cyclododecyl acrylate)	56710–66–8	310	DSC, onset, HR, 32 deg/min, quenched	1086
Poly(cyclohexyl acrylate) conventional		292		824
syndiotactic		289		
isotactic		285		

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Polymer	CAS No.	T_g(K)	Remarks	References
Poly(dodecyl acrylate)		270	Brittle point	821,829
Poly(2-ethoxycarbonylphenyl acrylate)		303		746
Poly(3-ethoxycarbonylphenyl acrylate)		297		746
Poly(4-ethoxycarbonylphenyl acrylate)		310		746
Poly(2-ethoxyethyl acrylate)		223		830
Poly(3-ethoxypropyl acrylate)		218		830,831
Poly(ethyl acrylate) conventional		249		23,634,775
syndiotactic		249		820,821,824
isotactic		248		832,833
Poly(2-ethylbutyl acrylate)		223	Brittle point	823
Poly(2-ethylhexyl acrylate)		223	Brittle point	821
Poly(ferrocenylethyl acrylate)		430	No experimental details	834
Poly(ferrocenylmethyl acrylate)		470–483	DSC heating rate	835
Poly(1H,1H-heptafluorobutyl acrylate)		243		155,836,837
Poly(1H,1H,3H-hexafluorobutyl acrylate)		251		836
Poly(2,2,2-trifluoroethyl acrylate)		263		836
Poly[2,2-difluoro-2-(2-heptafluorotetrahydrofuranyl) ethyl acrylate]		275	Brittle temperature	830
Poly(1H,1H-undecafluorohexyl acrylate)		234		836
Poly(fluoromethyl acrylate)		288	Estimated T_g	838
Poly(1H,1H-pentadecafluorooctyl acrylate)		256	Crystalline	836
Poly(5,5,6,6,7,7,7-heptafluoro-3-oxaheptyl acrylate)		228		830
Poly(1H,1H-undecafluoro-4-oxaheptyl acrylate)		205		830
Poly(1H,1H-nonafluoro-4-oxahexyl acrylate)		224		830
Poly(7,7,8,8-tetrafluoro-3,6-dioxaoctyl acrylate)		233		830
Poly(1H,1H-tridecafluoro-4-oxaoctyl acrylate)		205		830
Poly(2,2,3,3,5,5,5-heptafluoro-4-oxapentyl acrylate)		218		830,837
Poly(4,4,5,5-tetrafluoro-3-oxapentyl acrylate)		251		830
Poly(5,5,5-trifluoro-3-oxapentyl acrylate)		235		830
Poly(1H,1H-nonafluoropnetyl acrylate)		236		836
Poly(1H,1H,5H-octafluoropentyl acrylate)		238		836
Poly(heptafluoro-2-propyl acrylate)		278–283	No details on sample or measurement	839
Poly(1H,1H-pentafluoropropyl acrylate)		247		836
Poly(heptyl acrylate)		213	Brittle point	821
Poly(2-heptyl acrylate)		235	Brittle point	823
Poly(hexadecyl acrylate)		308	Brittle point	23,821,840,841
Poly(hexyl acrylate)		216	Brittle point	823
Poly(isobornyl acrylate) conventional		367		824
syndiotactic		369		
isotactic		363		
Poly(isobutyl acrylate)		249	Brittle point	823
Poly(isopropyl acrylate) conventional		267–270		746,823,824
syndiotactic		271–284		
isotactic		262		
Poly(1,2:3,4-di-O-isopropylidene-α-D-galactopyranos-6-O-yl acrylate)		371		11,842
Poly(magnesium acrylate)		673	Estimated from copolymer data	843
Poly(3-methoxybutyl acrylate)		217		844
Poly(2-methoxycarbonylphenyl acrylate)		319		746
Poly(3-methoxycarbonylphenyl acrylate)		311		746
Poly(4-methoxycarbonylphenyl acrylate)		340		746
Poly(2-methoxyethyl acrylate)		223		830
Poly(4-methoxyphenyl acrylate)		324		826
Poly(3-methoxypropyl acrylate)		198		830
Poly(methyl acrylate) conventional		283		18,22,23,81
		284	Dilatomer	1094
head to tail		278		576,720,775–777
head to head		304		821,824,831,841, 845–848
Poly(3,5-dimethyladamantyl acrylate)		379	DSC heating rate; data corrected (sci)	849,850
Poly(3-dimethylaminophenyl acrylate)		320		746
Poly(2-methylbutyl acrylate)		241	Brittle point	823
Poly(3-methylbutyl acrylate)		228	Brittle point	823

Polymer	CAS No.	T_g(K)	Remarks	References
Poly(methyl methacrylate)	9011-14-7			1102,1112
				1101,1107,1108
			DSC, onset, 16 deg/min HR, quenched, f (MW)	1101
			Dilatomer, CR 3 deg/h; creep relaxation, quenched	1109
atactic				1106
		378		1,17,22,25–27, 69,78,79,81,190, 201,263,286,287, 317,318, 352–354,400, 614,684,698,720, 775,777–779, 789,804,821,824, 846,858,860,862, 880,883–895
isotactic		311		6,122,720,824, 847,884,886,890, 895–901
syndiotactic		378		122,720,824,847, 890,895,896,898, 900,901
heterotactic		372	DSC, rapid cooling, 10 deg/min HR, onset point, Mn infinity	1103
Poly(trimethylsilyl methacrylate)isotactic		341	Heating rate 15 K/min, weak T_g for syndiotactic polymer	902
syndiotactic		400		
Poly[(2-nitratoethyl) methacrylate]		328		903
Poly(octadecyl methacrylate)		173		1,720,904
Poly(octyl methacrylate)		203,253	Conflicting data	23,695,821,840, 846,858
Poly(3-oxabutyl methacrylate)		289		846,857
Poly(3-oxa-5-hydroxypentyl methacrylate)		278–280	Mechanical method	880
Poly(pentyl methacrylate)		268	Brittle point	821
Poly(neopentyl methacrylate)	34903-87-2	299–312	DSC, f (HR)	1105
Poly(phenethyl methacrylate)		299		746
Poly(phenyl methacrylate)		383		353,746,820,847, 863,875
Poly(4-tert-butylphenyl methacrylate)	29696-27-3	371	DSC, f (HR)	1104
Poly(propyl methacrylate)		308	Conflicting data, 308–345 K reported	22,262,272,821, 847,857,858,860, 862,877,878,880
Poly(sodium methacrylate)		~583	Xp value	843
Poly(tetradecyl methacrylate)		201–264	Conflicting data	23,821,840,866

1.3.4 *Poly(methacrylamides)*

Polymer	CAS No.	T_g(K)	Remarks	References
Poly(4-butoxycarbonylphenylmethacrylamide)		401	Softening point	905
Poly(N-tert-butylmethacrylamide)		433	No experimental details	820
Poly(4-carboxyphenylmethacrylamide)		473	Softening point	905
Poly(4-ethoxycarbonylphenylmethacrylamide)		441	Softening point	905
Poly(4-methoxycarbonylphenylmethacrylamide)		453	Softening point	905

1.3.5 *Other α-and β-substituted Poly(acrylics) and Poly(methacrylics)*

Polymer	CAS No.	T_g(K)	Remarks	References
Poly(butyl butoxycarbonylmethacrylate)		298		906
Poly(butyl chlorocrylate)		330	Vicat softening point	863
Poly(sec-butyl chlorocrylate)		347	Vicat softening point	863
Poly(butyl cyanocrylate)		358		907
Poly(dibityl itaconate) see Poly(butyl butoxycarbonylmethacrylate)				
Poly(cyclohexyl chlorocrylate)		387	Vicat softening point	863
Poly(ethyl chloroacrylate)		366	Vicat softening point	832,863,908,909
10% isotactic		308	Calculated for infinite Mn; heating rate 20 K/min	
100% syndiotactic		404	Calculated for infinite Mn; heating rate 20 K/min	

Polymer	CAS No.	T_g(K)	Remarks	References
Poly(4-octanoylstyrene)		323	Mechanical method	728
Poly[4-(octyloxymethyl)styrene]		231	Dynamci method	736
Poly(2-octyloxystyrene)		286		769
Poly(4-octylstyrene)		228		738
Poly(2-pentyloxycarbonylstyrene)		365	Mechanical method	735
Poly(2-pentyloxymethylstyrene)		320	Mechanical method	729
Poly(2-phenethyloxymethylstyrene)		336	Mechanical method; viscosity low	729
Poly(2-phenoxycarbonylstyrene)		397	Mechanical method; viscosity low	742
Poly(4-phenoxystyrene)		~373	Softening point	83
Poly(4-phenylacetylstyrene)		351	Mechanical method	728
Poly(2-phenylaminocarbonylstyrene)		464	Mechanical method; viscosity low	742
Poly(4-phenylstyrene)		434	Extrapolated to zero rate	763,770
Poly(4-piperidinocarbonylstyrene)		387	Mechanical method	728
Poly[4-(3-piperidinopropionyl)styrene]		311	Mechanical method	754
Poly(4-propionylstyrene)		375	Mechanical method	728
Poly(2-propoxycarbonylstyrene)		381	Mechanical method	735
Poly(4-propoxycarbonylstyrene)		365	Mechanical method	728
Poly(2-propoxymethylstyrene)		370	Mechanical method; viscosity low	729
Poly(4-propoxymethylstyrene)		295	Dynamic method	736
Poly(4-propoxystyrene)		343	Mechanical method	737
Poly(4-propoxysulfonylstyrene) isotactic		490	DTA heating rate	771
Poly(styrene) isotactic and atactic		373		9,17,21,22,25, 47,51,57,63,64, 72,78,79,188, 190,191,261,263, 317,318 ,344, 350–352,394, 397,399,469,524, 569,576,619,628, 630,635,637,640, 646,647,6 84,699,731–734, 746,750,766,768, 772–810 1125,1133,1134, 1138,1139,1141
			DSC, onset, 16 deg/min HR, quenched, f (MW)	1126
			DSC, Mdp, 20 deg/min HR, f (MW)	1129
			DSC, Intg, f (HR,CR, MW)	1143
			DSC, Intg, f (HR,CR)	1144
			Dilatometer, CR 3 deg/ h; creep relaxation, quenched	1148
		368.2	Dilatometer, 2.5 deg/ min CR	1145
		371	DSC, onset, HR 32 deg/ min, quenched	1132
		371	DTA, DSC, onset, 1 deg/ min HR, f (HR)	1147
		371–377	DSC, penetration, onset MP, zero HR	1146
		373.5	DSC, Intg, OHR, 10 deg/ min CR	1142
		376	DSC, Mdp, 1 deg/min X HR,TH, f (MW)	1128
		377	DSC, onset, 20 deg/min HR after similar cool, f (MW)	1149